

CORRESPONDS TO
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(54) Inhibiting corrosion

(57) A method of inhibiting corrosion of iron and steel alloys in contact with oil-in-brine emulsions is claimed. The method comprises treating the oil-in-brine emulsions with an effective amount of a water soluble polymer having an average molecular weight of at least one million and an effective amount of a nitrogen-containing corrosion inhibitor.

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ENHANCED CORROSION PROTECTION BY
USE OF FRICTION REDUCERS IN CONJUNCTION WITH
CORROSION INHIBITORS

GB 2299331

INTRODUCTION

Field of the Invention

This invention relates to the prevention of corrosion in pipelines used for the transport of petroleum fluids.

5 Background of the Invention

Pipelines are commonly used for the transport of petroleum products, with steels as the most commonly used tubular materials for transport purposes. The pipe employed may range from four inches to over forty-eight inches in diameter, and have a minimum yield strength rating of 40,000 psi. Transported fluids may flow at velocities from 3 ft/sec
10 to over 60 ft/sec, and may cause pressures on the pipeline to be from atmospheric pressure to over 1,500 psi. These physical demands will have an effect on the constitution of the pipeline. Moreover, the presence of water and corrosive impurities in the petroleum products such as hydrogen sulfide, carbon dioxide and organic acids, leads to corrosion of the pipeline. The problem is particularly severe when the pipelines are used to transport
15 fluids at high flow velocities.

In the oilfield, brine, oil and gas make up the petroleum products which may travel through the pipe in separate phases or in a stable emulsion. Both conditions will be represented by the term oil-in-brine emulsion hereafter. Corrosion increases sharply as the salt content of the brine in the oil-in-brine emulsion increases to about 15% total dissolved
20 solids. Low pH brines tend to be more corrosive. Additional factors contributing to corrosion within the pipelines concern the makeup of the transported oil, which itself may

contain organic acids, paraffins, asphaltenes and aromatics. The gravity of the crude, the amount of acid gases, the salt content and composition all have an effect on corrosivity. Further, as temperature and pressure increase, they result in an increase in corrosion rate.

In order to protect the pipelines from this corrosive environment, it is now
5 common to treat the fluids transported by these pipelines with small quantities of corrosion inhibitors. Nitrogen-containing water-soluble molecules such as imidazoline salts as disclosed in DE 2846977 and polymerized fatty acids disclosed in U.S. Patent No. 4,197,091 are among the compounds which have been successfully employed as corrosion inhibitors. Other classes of corrosion inhibitors commonly used in petroleum production
10 include amides, amines, quaternary ammonium salts, nitrogen-containing heterocycles, and sulfur-containing compounds. Though several classes of corrosion inhibitors are known, it would be of great benefit to the art to increase the activity of corrosion inhibition additives.

Another factor which affects the transport of petroleum products, is friction
15 produced by turbulent flow as the petroleum products travel through the pipeline at high velocities. For example, in Prudhoe Bay, Alaska, the produced fluids travel inside 24 inch (61 cm) diameter multiphase pipelines from approximately 25 ft/sec to 50+ ft/sec depending upon production. The turbulence produced as the solutions are pumped through the pipe under pressure results in the production of friction. As a remedy, friction
20 reducing agents such as polymeric materials can be added to the stream to prevent consequent energy loss in the flow of the fluid as it travels through the pipeline. A good

friction reducer will cause a large decrease in friction at small concentrations, will be inexpensive, and will have high shear, temperature and pressure stability.

Water-soluble polymers such as polyacrylamide are known for reducing pipeline friction as disclosed in U.S. Patent No. 3,254,719, the specification of which is hereinafter incorporated by reference. Polyacrylamide has also been combined with dispersing agents, as disclosed in U.S. Patent No. 3,542,044 and with other co-polymers as disclosed in U.S. Patent No. 4,152,274. Generally, the polymers are injected continuously into the pipeline.

Acrylamide polymers, as the term is used herein, includes polymers consisting entirely of acrylamide units, which may be partially hydrolyzed to acrylic acid units. The term acrylic acid units encompasses the various salts such as the sodium or potassium salt form of the acrylic acid. This hydrolysis of amide groups to carboxylic acid groups may be conducted using alkaline materials such as sodium hydroxide, ammonium hydroxide, soda ash, potassium hydroxide, or quaternary ammonium hydroxide. Optimum partial hydrolysis of polyacrylamide for operation as a friction loss reducer is described in U.S. Patent No. 3,254,719 as 20 to 40 percent hydrolysis of available amide groups.

Polyacrylamide may be synthesized as one of three forms: solid, solution or emulsion. Dry polymer may be obtained by solution polymerization with a high concentration of monomer. The resultant gel can be ground and dried to obtain polyacrylamide in a powdered form. Solution polymerization with up to 15% monomer results in an aqueous solution of polyacrylamide. Lastly, polyacrylamide can be made in the form of an aqueous water-in-oil emulsion. The emulsion is formed by utilizing a water-in-oil emulsifying agent. To this monomer is added a free radical-type

polymerization catalyst and then heat is applied under free radical-forming conditions to form water-soluble polymer lattices. The polymer lattices may be unstable, and therefore must be treated with additional emulsifiers. The preparation of these emulsions is described in U.S. Patent No. 3,284,393. Subsequently, the emulsions may be inverted to produce aqueous solutions.

Another class of water-soluble polymers useful in this invention are water-soluble cationic polymers dispersed in aqueous solutions of inorganic salts. The inorganic salt may be a sulfate, a chloride or a phosphate, but is preferably ammonium sulfate. Cationic monomers such as dimethylaminoethyl acrylate, dimethylaminoethyl methacrylate methyl chloride quaternary salt and dimethylaminoethyl methacrylate benzyl chloride quaternary salt may be used to form dispersed homopolymers. Alternatively the cationic monomers described above can be co-polymerized with acrylamide, or ter-polymers may be formed by combinations of cationic monomers with acrylamide.

It is therefore an object of the invention to provide the art a superior method for enhancing the effect of corrosion inhibitors in pipelines transporting oil-in-brine emulsions.

Summary of the Invention

We have found that water soluble co-polymers, especially co-polymers of acrylamide and acrylic acid, can enhance the activity of corrosion inhibitors in brine solutions by decreasing turbulence such that the corrosion inhibitor can more thoroughly contact the internal surface of the pipeline. Therefore, the friction flow reducing agent acts synergistically with corrosion inhibitors to increase their efficiencies. The result is

that the inhibitors can be injected into the pipeline at much lower concentrations, which is both an economical and environmental advantage.

The Invention

The basic method of the invention is to prevent corrosion of the metallic surfaces of a pipeline in contact with an oil-in-brine emulsion of produced fluids being transported under turbulent flow conditions comprising adding to the oil-in-brine emulsion flowing through the pipeline an effective amount of a water-soluble polymer having an average molecular weight greater than one million and an effective amount of a nitrogen-containing corrosion inhibitor.

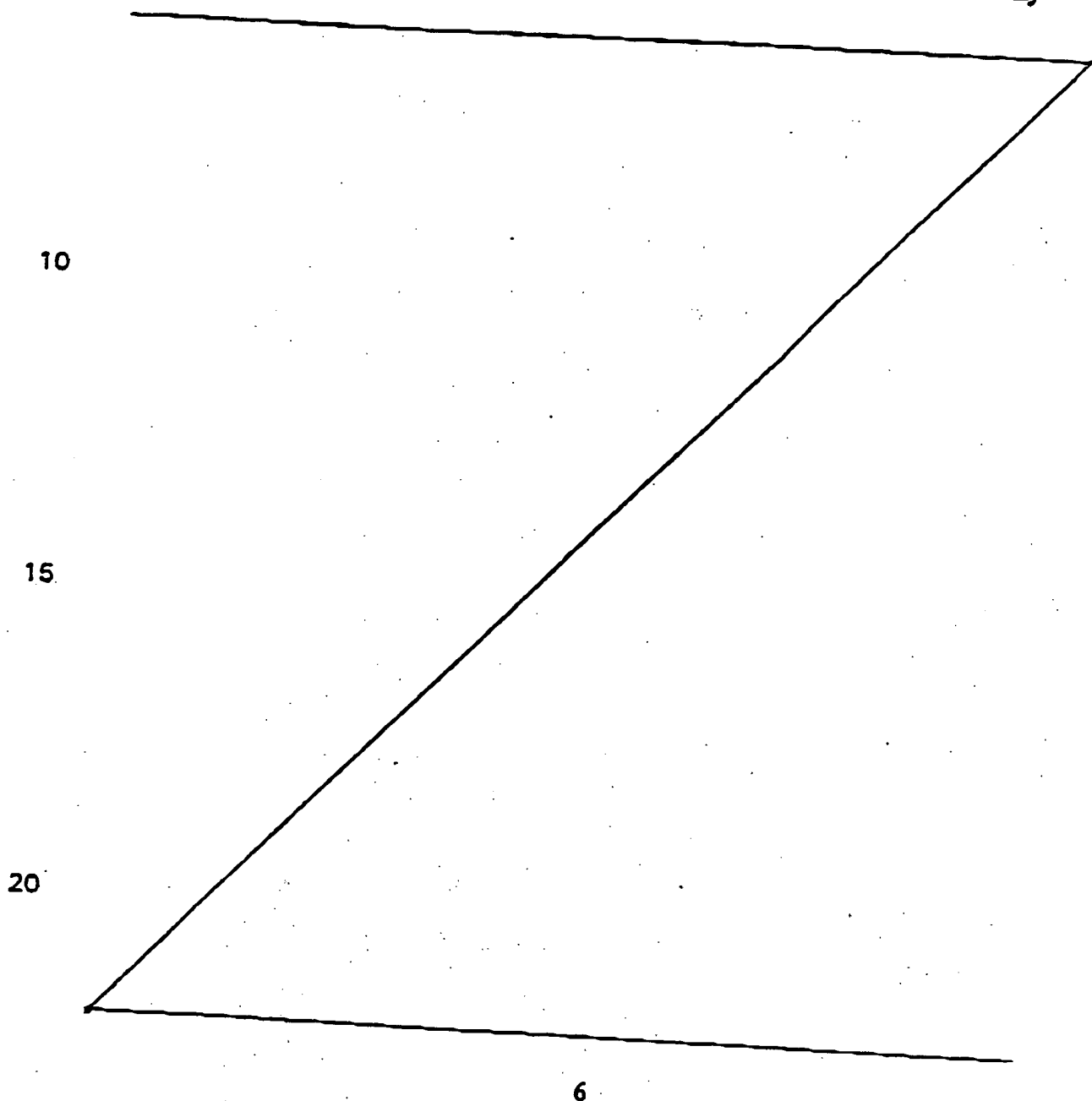
The present invention relates to reduction of corrosion by concomitant reduction in turbulent flow in a pipeline for the transport of oil-in-brine emulsions. Suitable friction-reducing polymers may include, but are not limited to: water soluble anionic, non-ionic, and cationic polymers.

The present invention provides a method for preventing corrosion of the metallic surfaces of a pipeline in contact with an oil-in-brine emulsion of a crude oil being transported under turbulent flow conditions characterized by adding to the oil-in-brine emulsion flowing through the pipeline

- A. an effective amount of a water-soluble polymer having an average molecular weight greater than one million and
- B. an effective amount of a nitrogen-containing corrosion inhibitor.

The anionic treatment polymers useful in the practicing of this invention may be homopolymers of acrylic acid, methacrylic acid or maleic anhydride and copolymers containing acrylic acid, or methacrylic acid, which copolymers also contain at least one of the monomers

- chosen from the group consisting of acrylamide, methacrylamide, malic anhydride, hydroxypropylacrylates, hydroxyethylacrylates, N-tertiary butyl acrylamide, 2-acrylamido-2-methylpropane sulfonate, sulfomethyl acrylamide, sulfomethyl methylacrylamide, sulfoethylacrylamide, sulfonated styrene, vinyl sulfonate, itaconic acid, or N-
- 5 hydroxypropylacrylamide. Useful dispersion polymers may be obtained commercially



from the Hymo Corporation, Japan. Cationic water-soluble polymers may be synthesized from monomers of methacrylate, acrylate or methacrylamide quaternary salts, or diallyldimethylammonium chlorid as homopolymers or as co-polymers with acrylamide. Non-ionic water soluble polymers may be homopolymers of acrylamide or co-polymers of
5 acrylamide and other suitable monomers. Water soluble co-polymers of acrylamide and acrylic acid with from 5 to 95% by weight acrylamide are presently preferred.

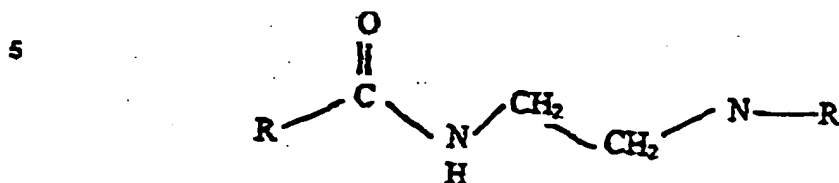
One aspect of the invention is to use a water-soluble co-polymer with a molecular weight from 100,000, where the upper limit of the molecular weight will be limited only by the solubility of the polymer in solution. Further, the water soluble co-polymer will have a
10 molecular weight of at least one million. Preferentially, the water-soluble polymer will have a molecular weight of at least five million. The polymer may be added to the oil-in-brine emulsion continuously in an amount of from 25 to 2500 ppm based on the oil-in-brine emulsion. Alternatively, the polymer may also be added to the oil-in-brine emulsion continuously in an amount of from 50 to 1000 ppm based on the oil-in-brine emulsion.
15 Preferentially, the polymer is added continuously to the oil-in-brine emulsion in an amount of from 100 to 300 ppm based on the oil-in-brine emulsion.

The water-soluble polymer can be in powdered form, in the form of a dispersion, or in the form of a solution.

Corrosion inhibitors are enhanced by injection of friction flow reducers into the
20 pipeline, though other oilfield pipeline additives may also have enhanced activity when used in conjunction with friction flow reducers. These other additives include: emulsion breakers, antifoams, scale inhibitors, H₂S and O₂ scavengers, biocides and paraffin/

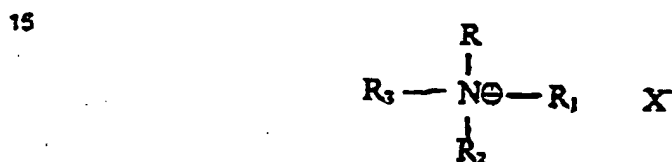
asphaltene inhibitors. Preferentially, the corrosion inhibitor is a quaternary ammonium salt, alkyl-substituted heterocycle, amide or an imidazoline.

A corrosion inhibitor useful in this invention is an amide of the following structure:



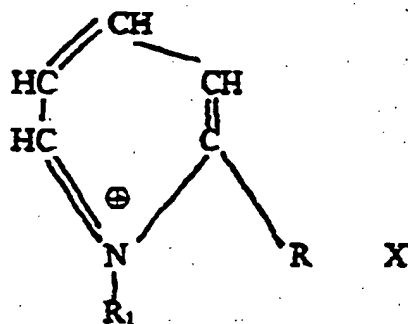
10 where R is a moiety containing eight to twenty carbon atoms selected from the group consisting of saturated and unsaturated alkyls and R₁ is an alkyl polyamine carboxylic acid salt moiety having one to twenty carbon atoms.

Another corrosion inhibitor useful in this invention is a quaternary ammonium salt of the following structure:



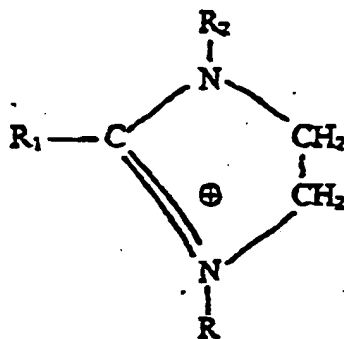
wherein R, R₂, and R₃ are moieties containing one to twenty-two carbon atoms and R₁ is a moiety containing one to twenty-two carbon atoms and is an alkyl, aryl or alkylaryl group
20 and X is an anion.

A third type of corrosion inhibitor useful in this invention is an alkyl substituted heteroaromatic of the following structure:



wherein R is an alkyl moiety containing one to twenty-two carbon atoms and R₁ is a moiety containing one to twenty-two carbon atoms and is an alkyl or alkylaryl group and X is an anion.

A fourth type of corrosion inhibitor useful in this invention is an imidazoline of the following structure:



wherein R is a moiety selected from the group consisting of benzyl, methyl, and carboxylic acid salts, R₁ is an alkyl moiety containing one to twenty-two carbon atoms and R₂ is a moiety selected from the group consisting of alkyl polyamines having one to twenty-two carbon atoms, hydrogen and alcohols having one to twenty carbon atoms. The imidazoline is oil-soluble, and it is believed that upon exposure to water, it hydrolyzes to some extent to an amide.

In one aspect of the invention, the chosen corrosion inhibitor is injected continuously into the pipeline in an amount of from 25 to 2500 ppm. Moreover, the chosen corrosion inhibitor may also be injected continuously into the pipeline in an amount of from 50-1000 ppm. Preferentially, the chosen corrosion inhibitor is injected
5 continuously into the pipeline in an amount of from 100 to 200 ppm.

EXPERIMENTS

Testing System

The polymer and corrosion inhibitor combination of the invention was tested in a recirculating flow loop system. This device is described in the literature in some detail in
10 an article by Shi-Lang Fu and J. Byron Strickland entitled "Corrosion Study in Dynamic High Velocity Flow Application Based on New Flow Loop Data," Corrosion/93, paper No. 117, NACE, Houston, TX (1993).

Briefly, the device comprises three 1 inch O.D. stainless steel lines, an autoclave 25 a fluid reservoir, a high horsepower centrifugal pump and many process regulating
15 devices. Sampling is effected by carbon steel coupons mounted on specimen holders placed vertically in the center of the flow stream, mounted at different locations within the pipe such that test fluids flow through the annular space between the coupons and the pipe inner wall.

The test fluid is a mixture which consists of 5% NaCl solution and kerosene in a
20 80/20 ratio, to simulate oilfield conditions. Oxygen was expelled from the flow loop and as well as from the synthetic brine solution (through CO₂ sparging) prior to each test.

Test fluids were pre-heated to an operating temperature of 74°C, and an operating pressure of 35 psi was utilized. A pre-determined amount of the polymer and corrosion inhibitor combination was injected into the flow loop. This amount was calculated based on the total fluid volume to give the same concentration as would be used in the field.

- 5 Since the flow loop is a closed system, the concentration of inhibitors in the fluid remains unchanged. This is equivalent to a continuous injection of inhibitor into the pipeline.

The test consisted of treating the test fluids with the test inhibitor/polymer combination and recirculating the resulting solution under pressure through the flow loop system for several hours at the operating temperature. Three different velocities were
10 used for testing each polymer and/or water-soluble corrosion inhibitor. Following each test, the coupons were removed and the corrosion products were scraped from the surface. The corrosion rate was determined from the measured weight loss of the test coupons.

Example 1

- 15 Samples of various water-soluble polymers were evaluated in the flow loop system described earlier with results as reported in Table I. Each polymer was tested at a dosage of 150 ppm. A lower corrosion rate number indicates that some inhibition of the corrosion process has occurred. As illustrated by Table I, the anionic latex demonstrated the greatest corrosion inhibition, but the cationic and dispersion polymers also reduced
20 corrosion to a certain extent. These results can be compared to data from two blank reactions, illustrated by rows one and two. There, much higher corrosion rates were evident than when the various polymers were added.

TABLE I

Polymer	Polymer Family	Corrosion Rates (mpy)		
		Velocity I 8.0-8.3 ft/sec	Velocity II 1.8-12.0 ft/sec	Velocity III 15.7-15.8 ft/sec
none	none	735	867	784
none	none	925	963	959
Acrylamide/Acrylic Acid co-polymer (70/30) ²	Anionic Latex ¹	236	265	249
A ³	Cationic Latex ²	659	727	638
B ⁴	Dispersion Polymer	623	726	620

¹ latex refers to an oil-in-water emulsion

² mole weight ratio

³ A = dimethylaminoethyl acrylate benzyl sulfate quaternary salt/acrylamide copolymer (54/46 mole ratio)

⁴ B = dimethylaminoethyl benzyl chloride quaternary salt/dimethylaminoethyl methyl chloride quaternary salt/acrylamide copolymer (25/10/65 mole ratio)

Example 2

The 70/30 mole weight ratio acrylamide/acrylic acid copolymer was tested in the presence of various corrosion inhibitors using the flow loop system described above, with results as reported in Table II. In each case, there is a much greater amount of inhibition when the water soluble polymer is added in conjunction with a corrosion inhibitor than with the corrosion inhibitor alone. The synergy of the use of the corrosion inhibitor in conjunction with a friction flow reducer is evident at each of the three tested velocities.

Row seven illustrates a blank experiment in which neither corrosion inhibitor nor water soluble polymer were added, to establish initial rates of corrosion. Those values were in the range of 700-800 mpy. For comparison purposes, corrosion reduction by water soluble co-polymer alone is listed in row eight. Dramatic reductions of corrosion rates

from 700-800 mpy to 30-50 mpy are obtained by the practice of this invention, the combination of water soluble co-polymers and corrosion inhibitors.

TABLE II

Inhibitor Type	Inhibitor Dosage ppm	Acrylamide/Acrylic Acid Co-polymer ¹ Dosage ppm	Corrosion Rates (mpy)		
			Velocity I 8.2 ft/sec	Velocity II 12.0 ft/sec	Velocity III 15.7 ft/sec
A	100	150	79	80	86
A	100	none	346	583	660
B	170	170	52	57	45
B	100	none	413	458	526
C	50	150	48	36	45
C	50	none	64	95	197
none	none	none	735	867	784
none	none	none	925	963	959
none	none	150	236	265	249

¹70/30 mole weight ratio

5 A = carboxylic acid salts of polyamidoamines

B = mixture of Alkyl Pyridine benzyl chloride quaternary salt and imidazoline quaternary salt

C = acrylic acid adduct of imidazoline

Example 3

The water-soluble cationic dispersion polymers were tested in the presence of a corrosion inhibitor using the flow loop system described above, with results as reported in Table III.

Row four illustrates a blank experiment in which neither corrosion inhibitor nor water soluble polymer were added, to establish initial rates of corrosion. Those values were in the range of 900-1100 mpy. For comparison purposes, corrosion reduction by the

corrosion inhibitor in the absence of friction flow reducing water soluble co-polymer is listed in row three. Row two shows that cationic dispersion polymer A in combination with the corrosion inhibitor increases the corrosion reduction over corrosion inhibitor alone. Thus, this polymer demonstrates the synergy of friction flow reducers and

5 corrosion inhibitors.

TABLE III

Polymer	Polymer Dosage ppm	Inhibitor	Inhibitor Dosage ppm	Corrosion Rates (mpv)		
				8.2 ft/sec	12 ft/sec	15.7 ft/sec
A	150 ppm	B	100 ppm	202	214	231
C	150 ppm	B	100 ppm	644	681	676
None	0 ppm	B	100 ppm	413	458	526
None	0 ppm	None	0 ppm	964	1035	1098

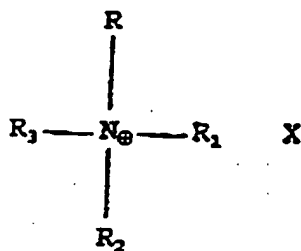
A= cationic dispersion polymer, 54% dimethylaminoethyl methacrylate (sulfonic acid salt) and 46% acrylamide

B= mixture of Alkyl Pyridine benzyl chloride quaternary salt and imidazoline quaternary salt

10 C= cationic dispersion polymer, 65% acrylamide, 25% dimethylaminoethyl acrylate benzyl chloride quaternary, 10% dimethylaminoethyl acrylate methyl chloride quaternary

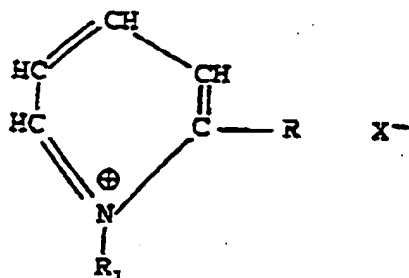
CLAIMS

1. A method for preventing corrosion of the metallic surfaces of a pipeline in contact with an oil-in-brine emulsion of a crude oil being transported under turbulent flow conditions characterized by adding to the oil-in-brine emulsion flowing through the pipeline
 - A. an effective amount of a water-soluble polymer having an average molecular weight greater than one million and
 - B. an effective amount of a nitrogen-containing corrosion inhibitor.
2. The method of claim 1 characterized in that the water-soluble polymer is selected from the group consisting of polyacrylamide and co-polymers of acrylamide and acrylic acid having from 5-95% by weight acrylamide, said polymer having an average molecular weight greater than five million.
3. The method of claim 2 characterized in that from 25 to 2500 ppm of the polymer is added to the oil-in-brine emulsion.
4. The method of claim 3 characterized in that from 25 to 2500 ppm of the corrosion inhibitor is added to the oil-in-brine emulsion and the corrosion inhibitor is selected from the group consisting of quaternary ammonium salts, alkyl-substituted heterocyclics, amides and imidazolines.
5. The method of claim 4 characterized in that the quaternary ammonium salt has the following structure:



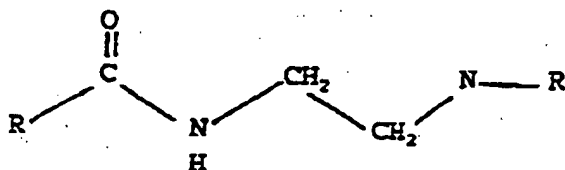
where R, R₁, R₂ and R₃ are moieties containing one to twenty-two carbon atoms selected from the group consisting of alkyl, aryl and alkylaryl groups and X is an anion.

6. The method of claim 4 characterized in that the alkyl-substituted heterocyclic has the following structure:



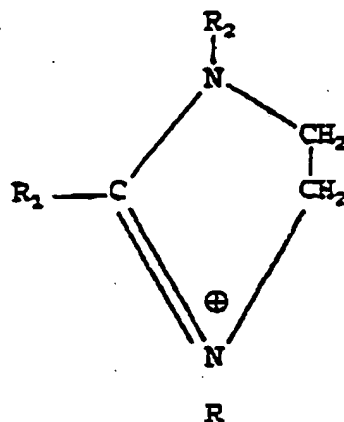
where R is an alkyl moiety containing one to twenty-two carbon atoms and R₁ is a moiety containing one to twenty-two carbon atoms selected from the group consisting of alkyl and alkylaryl and X is an anion.

7. The method of claim 4 characterized in that the amide has the following structure:



where R is a moiety containing eight to twenty carbon atoms selected from the group consisting of saturated and unsaturated alkyls and R₁ is an alkyl polyamine carboxylic acid salt moiety having one to twenty carbon atoms.

8. The method of claim 4 characterized in that the imidazoline has the following structure:

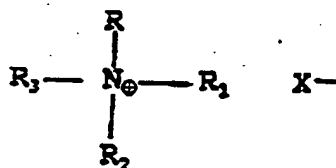


wherein R is a moiety selected from the group consisting of benzyl, methyl and carboxylic acid salts, R₁ is an alkyl moiety containing one to twenty-two carbon atoms and R₂ is selected from the group consisting of alkyl polyamines having one to twenty-two carbon atoms, hydrogen and alcohols having one to twenty carbon atoms.

9. The method of claim 2 characterized in that from 50-1000 ppm of the polymer is added to the oil-in-brine emulsion.

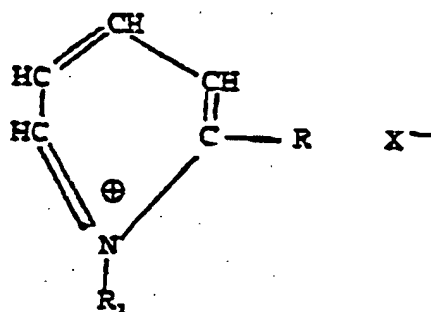
10. The method of claim 9 characterized in that from 50-1000 ppm of a corrosion inhibitor is added to the oil-in-brine emulsion and the corrosion inhibitor is selected from the group consisting of quaternary ammonium salts, alkyl-substituted heterocyclics, amides and imidazolines.

11. The method of claim 10 characterized in that the quaternary ammonium salt has the following structure:



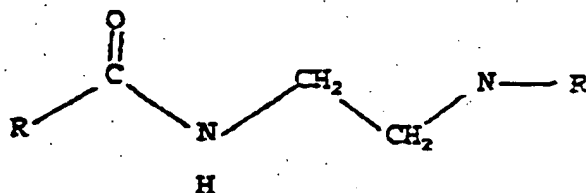
where R, R₁, R₂ and R₃ are moieties containing one to twenty-two carbon atoms selected from the group consisting of alkyl, aryl and alkylaryl groups and X is an anion.

12. The method of claim 10 characterized in that the alkyl-substituted heterocyclic has the following structure:



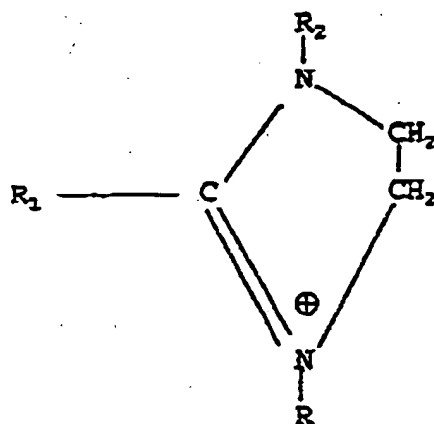
where R is an alkyl moiety containing one to twenty-two carbon atoms and R₁ is a moiety containing one to twenty-two carbon atoms selected from the group consisting of alkyl and alkylaryl and X is an anion.

13. The method of claim 10 characterized in that the amide has the following structure:



where R is a moiety containing eight to twenty carbon atoms selected from the group consisting of saturated and unsaturated alkyls and R₁ is an alkyl polyamine carboxylic acid salt moiety having one to twenty carbon atoms.

14. The method of claim 10 characterized in that the imidazoline has the following structure:

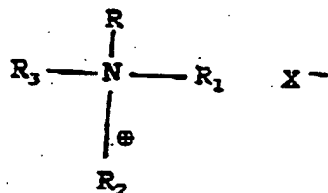


wherein R is a moiety selected from the group consisting of benzyl, methyl and carboxylic acid salts, R₁ is an alkyl moiety containing one to twenty-two carbon atoms and R₂ is a moiety selected from the group consisting of alkyl polyamines having one to twenty-two carbon atoms, hydrogen and alcohols having one to twenty carbon atoms.

15. The method of claim 2 characterized in that from 100-300 ppm of the water soluble polymer is added to the oil-in-brine emulsion.

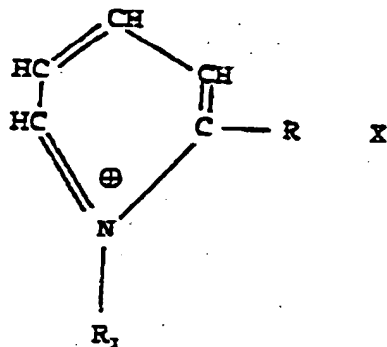
16. The method of claim 15 characterized in that from 100-200 ppm of the corrosion inhibitor is added to the oil-in-brine emulsion and the corrosion inhibitor is selected from the group consisting of quaternary ammonium salts, alkyl-substituted heterocycles, amides and imidazolines.

17. The method of claim 16 characterized in that the quaternary ammonium salt has the following structure:



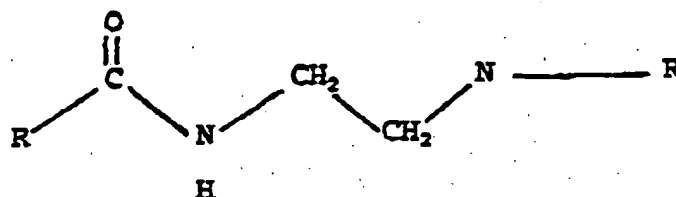
where R, R₁, R₂ and R₃ are moieties containing one to twenty-two carbon atoms selected from the group consisting of alkyl, aryl and alkylaryl groups and X is an anion.

18. The method of claim 16 characterized in that the alkyl-substituted heterocyclic has the following structure:



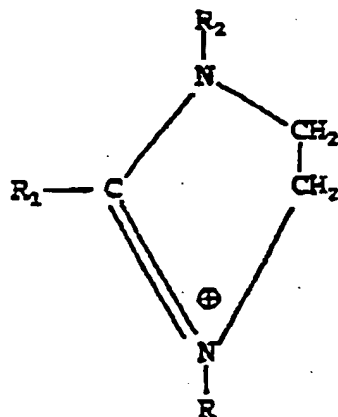
where R is an alkyl moiety containing one to twenty-two carbon atoms and R₁ is a moiety containing one to twenty-two carbon atoms selected from the group consisting of alkyl and alkylaryl and X is an anion.

19. The method of claim 16 characterized in that the amide has the following structure:



where R is a moiety containing eight to twenty carbon atoms selected from the group consisting of saturated and unsaturated alkyls and R₁ is an alkyl polyamine carboxylic acid salt moiety having one to twenty carbon atoms.

20. The method of claim 16 characterized in that the imidazoline has the following structure:



wherein R is a moiety selected from the group consisting of benzyl, methyl and carboxylic acid salts, R₁ is an alkyl moiety containing one to twenty-two carbon atoms and R₂ is a moiety selected from the group consisting of alkyl polyamines having one to twenty-two carbon atoms, hydrogen and alcohols having one to twenty carbon atoms.

21. A method substantially as herein described with particular reference to the examples.

**Patent
Office**22

Application No: GB 9606008.2
Claims searched: 1-21

Examiner: Roy Honeywood
Date of search: 9 July 1996

**Patents Act 1977
Search Report under Section 17**

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:
UK CI (Ed.O): C1C
Int CI (Ed.6): C23F 11/173
Other: ONLINE: WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
	None	

X Document indicating lack of novelty or inventive step
Y Document indicating lack of inventive step if combined with one or more other documents of same category.
& Member of the same patent family

A Document indicating technological background and/or state of the art.
P Document published on or after the declared priority date but before the filing date of this invention.
E Patent document published on or after, but with priority date earlier than, the filing date of this application.